

# Exact ground state density functional theory for impurity models coupled to external reservoirs and transport calculations

Peter Schmitteckert<sup>1</sup> and Ferdinand Evers<sup>1,2</sup>

<sup>1</sup>*Institut für Theorie der Kondensierten Materie, Universität Karlsruhe, D-76128 Karlsruhe, Germany*

<sup>2</sup>*Institut für Nanotechnologie, Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Germany*

(Dated: February 1, 2008)

A method is presented, which employs the density matrix renormalization group technique in order to construct exact ground state exchange correlation functionals for models of correlated electron systems coupled to external reservoirs. The technique is applied to the  $M$ -site resonant level model. We calculate its exact Kubo-conductance, which is available within DMRG, and compare to the single-particle conductance obtained from Kohn-Sham energies and orbitals of the exact ground state density functional theory (DFT). It is found that the position of transport resonances is reproduced essentially exactly, while deviations in the level broadening can be less than 1% and do not exceed 10%. Our findings lend strong support to a recently held point of view, namely that approximations in the ground state functionals used in DFT based transport calculations can lead to drastic errors in transport calculations while exchange correlation contributions to the induced effective potential tend to be less significant.

PACS numbers: 31.15.Ar, 71.15.Mb, 81.07.Nb

Running an electrical current through individual molecules and being able to control the current flow by molecular design is one of the intriguing aspects of Molecular Electronics. Naturally, the interesting behavior of such “devices” is frequently related to specific properties of the molecule at hand. Therefore, in order to properly understand experimental findings, notably the current voltage characteristics, ab initio calculations play a key role in this field.

The challenge in such ab initio calculations for transport properties is to accurately describe interaction effects on the junction together with wavefunction hybridization with the contacts. To deal with the latter, it is mandatory to treat a sizable part of the contact on the same footing as the molecule. To achieve sufficient system sizes, the current “standard method” is based on the density functional theory (DFT). [1, 2, 3]

A justification of the principal approach, namely the use of the single particle Keldysh formalism in conjunction with the Kohn-Sham (KS) scheme of time dependent (TD) DFT, has been proposed in Ref. [2] on a heuristic level and by Stefanucci and Almbladh has been based on a detailed analysis using the Keldysh-technique. [4]

In practical calculations approximate exchange correlation (XC) functionals have to be employed. Consequences of such approximations have been investigated in Ref. [5], where a relation between the linear current  $\mathbf{j}$ , the KS-Kubo-conductivity and the TDDFT functional  $\mathbf{E}_{\text{xc}}(\mathbf{r}\omega)$  has been derived:

$$\mathbf{j}(\mathbf{r}\omega) = \int d^3r' \hat{\sigma}_s[n_0](\mathbf{r}\mathbf{r}') (\mathbf{E}_{\text{tot}}(\mathbf{r}'\omega) + \mathbf{E}_{\text{xc}}(\mathbf{r}'\omega)). \quad (1)$$

( $\mathbf{E}_{\text{tot}}(\mathbf{r}\omega)$  denotes the sum of external and Hartree field,  $n_0(\mathbf{r})$  the ground state electron density.) In one dimension and the  $dc$ -limit,  $j(\mathbf{r}, \omega \rightarrow 0) = I$ , so Eq. (1) reduces to  $I = g_s (V_{\text{tot}} + V_{\text{XC}})$  introducing the KS-conductance,  $g_s$ , the physical voltage  $V_{\text{tot}}$  and its XC-shift  $V_{\text{XC}}$  [5].

In most current implementations of the standard method, the linear current response derives from calculating  $g_s$  in a local density approximation. Moreover, the XC-terms,  $V_{\text{XC}}$  or  $\mathbf{E}_{\text{xc}}$ , are universally ignored even though  $\mathbf{E}_{\text{xc}}(\omega)$  is generally important for the calculation of excitation energies [6]. Such approximations must be expected to have severe consequences. Most notably, the missing derivative discontinuity in available XC-functionals can artificially boost the DFT level broadening  $\Gamma_{\text{DFT}}$  observed in the variation of  $g_s$  with the gate voltage,  $V_{\text{gate}}$ , from its true value  $\Gamma$  up to the interaction energy  $U \gg \Gamma$  and thus completely impair an accurate prediction of transport coefficients [8]. This effect is a major suspect to cause much of the strong deviations that are frequently observed between theoretical and experimentally determined transport coefficients. [5, 9, 10]

Further analysis of Eq. (1) has been impaired by the fact, that for correlated molecular systems, which have been coupled to external reservoirs, exact XC functionals are not available. To overcome this fundamental barrier, we put forward a general idea in this work, namely to marry DFT with the density matrix renormalization group (DMRG) technique. Our approach allows to construct exact ground state (GS) functionals for a broad class of generic model systems of correlated fermions including external reservoirs. Here, we apply this method to obtain the exact KS conductance  $g_s$ . By comparing to the exact physical conductance,  $g = I/V_{\text{tot}}$ , it is demonstrated that  $g_s$  gives a highly accurate estimate for position and broadening of transport resonances implying that dynamical corrections  $V_{\text{XC}}$ , including the viscous part [11], are small. We show this specifically for the interacting resonant level model (IRLM) and the resonant chain model under conditions of the Coulomb blockade. Arguments are given, why we expect our results to be more generally valid.

The IRLM and its extension including reservoirs, that

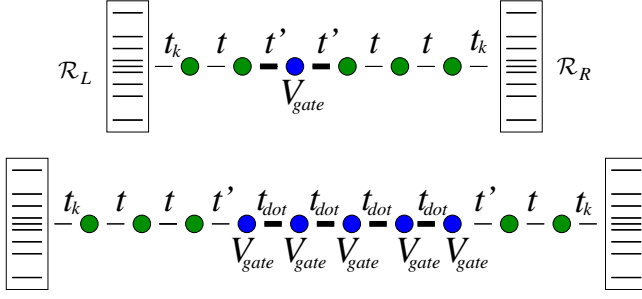


FIG. 1: (Color online) Schematic representation of the calculational setup. Filled circles indicate the extended molecule,  $e\mathcal{M}$ . Gate voltage,  $V_{\text{gate}}$ , is applied to molecule (dot),  $\mathcal{M}$ , only. Interacting sites are coupled by fat line links. Link labels indicate hopping amplitudes in the leads  $t$ , on the molecule  $t_{\text{dot}}$  and near the contacts  $t'$  and  $t_k$ . ( $t=1, t_{\text{dot}}=0.5$  in all calculations presented.)  $\mathcal{R}_L, \mathcal{R}_R$  denotes the reservoirs, here in  $k$ -space representation. Upper panel: single site resonance level model. Lower panel: five site model.

we employ in this work, is a suitable testbed to study strong correlation effects on transport. The model Hamiltonian reads  $\mathcal{H} = \mathcal{H}_{e\mathcal{M}} + \mathcal{H}_U + \mathcal{H}_{\mathcal{R}} + \mathcal{H}_T$ , with

$$\mathcal{H}_{e\mathcal{M}} = V_{\text{gate}} \sum_{\ell \in \mathcal{M}} \hat{c}_{\ell}^{\dagger} \hat{c}_{\ell} - \sum_{\ell, \ell-1 \in e\mathcal{M}} (t_{\ell} \hat{c}_{\ell}^{\dagger} \hat{c}_{\ell-1} + \text{h.c.}) \quad (2)$$

$$\mathcal{H}_U = U \sum_{\ell, \ell-1 \in \mathcal{M}} \left( \hat{n}_{\ell} - \frac{1}{2} \right) \left( \hat{n}_{\ell-1} - \frac{1}{2} \right), \quad (3)$$

where  $\hat{c}_{\ell}^{\dagger}$  ( $\hat{c}_{\ell}$ ) and  $\hat{c}_{\ell}$  ( $\hat{c}_{\ell}$ ) are spinless fermionic creation and annihilation operators at site  $\ell$  (at momentum  $k$ ),  $\hat{n}_{\ell} = \hat{c}_{\ell}^{\dagger} \hat{c}_{\ell}$ . Furthermore,  $\mathcal{H}_{\mathcal{R}} = \sum_{k \in \mathcal{R}_L, \mathcal{R}_R} \epsilon_k \hat{c}_k^{\dagger} \hat{c}_k$  and

$$\mathcal{H}_T = - \left( \sum_{k \in \mathcal{R}_L} t_k \hat{c}_k^{\dagger} \hat{c}_1 + \sum_{k \in \mathcal{R}_R} t_k \hat{c}_k^{\dagger} \hat{c}_{M_E} \right) + \text{h.c.} \quad (4)$$

Indices denote Hilbert spaces of the molecule proper (nanostructure/quantum dot),  $\mathcal{M}$ , of the extended molecule,  $e\mathcal{M}$  and of the left and right electrode reservoirs,  $\mathcal{R}_L, \mathcal{R}_R$ .  $\mathcal{H}_T$  denotes the tunneling Hamiltonian describing the contact between reservoirs and the extended molecule; the interaction on the molecule is modeled by  $\mathcal{H}_U$ . ( $U=2t$  in all calculations presented.) The indices 1 and  $M_E$  denote the first and last site in  $e\mathcal{M}$ . The general setup is displayed in Fig. 1. For the single level model the interaction  $U$  extends on the link between the resonant level and the neighboring lead sites. In all calculations we have considered the case of a half filled band and zero temperature,  $E_{\text{Fermi}}=0, T=0$ .

We calculate the GS of our model Eq. (2) by means of a DMRG calculation. DMRG[12, 13] is a method that searches for an optimized subspace of the complete Hilbert space in which selected many body states can be described accurately. Notice, that our setup include the leads in momentum space representation,  $\mathcal{H}_{\mathcal{R}}$ , which is non-standard, but crucial for later transport calculations, Fig. 1; for details see.[14] In this way we obtain the local electron density on  $e\mathcal{M}$  together with the occupation

number of lead levels. Typically, we use more than 1300 states per block and ten finite lattice sweeps.

Next, we briefly explain how an exact DFT may be constructed generalizing earlier ideas by Gunnarsson and Schönhammer.[15] We define a KS-Hamiltonian  $\mathcal{H}_s = \mathcal{H}_0 + V_{\text{HXC}}$ , with  $\mathcal{H}_0 = \mathcal{H}_{e\mathcal{M}} + \mathcal{H}_{\mathcal{R}} + H_T$  (free fermions) and an XC potential  $V_{\text{HXC}} = \sum_j v_j \hat{n}_j$  also including the Hartree term. Here,  $n_j$  denotes the particle density. The sum is over the lattice sites  $\ell$  of  $e\mathcal{M}$  and the states  $k$  of  $\mathcal{R}$ . According to theorems by Kohn and Hohenberg[16] and Kohn and Sham[17] a unique set of coefficients  $v_j$  specifying the XC kernel exists, such that the KS-particle density coincides with the exact density of the many body GS. In practice, we find  $v_j$  solving a standard optimization problem, which yields a final relative density mismatch of less than  $10^{-10}$  per site.

Within DMRG the linear conductance can be obtained from evaluating the Kubo-formula [14, 18]

$$g = \frac{8\pi e^2}{h} \langle \Psi_0 | \hat{J}_{n_1} \frac{\eta(\mathcal{H} - E_0)}{[(\mathcal{H} - E_0)^2 + \eta^2]^2} \hat{J}_{n_2} | \Psi_0 \rangle, \quad (5)$$

where  $|\Psi_0\rangle$  is the many body ground state,  $\eta$  is the broadening parameter.  $J_n$  is the current density operator at the bond between site  $n$  and  $n-1$  and  $E_0$  denotes the GS energy. Due to particle number conservation, the dc-conductance is independent of  $n_1, n_2$ . For the details of the procedure see Ref. [14, 18].

The conductance  $g$  – as in fact any dynamical correlator at  $T=0$  – can be calculated evaluating proper GS matrix elements of certain known many body operators, see e. g. Eq. (5). Therefore, the general principles of DFT apply and functionals exist, parameterized by  $\eta$  (or frequency  $\omega$ , times  $t, t'$  etc.), which allow to calculate such correlators from the GS density  $n_0$  alone. The functional, which would yield the exact conductance  $g[n_0]$  is not known. An approximative expression for  $g$  coinciding with the exact KS conductance  $g_s$  is readily obtained employing Eq. (5) using the KS ground state with KS single particle energies  $\epsilon_p$ , the corresponding orbitals for evaluating the matrix elements  $J_{0p}$  and  $\mathcal{H} \rightarrow \mathcal{H}_s$

$$g_s = \frac{8\pi e^2}{h} \sum_{p,q} \frac{J_{0p} J_{q0} \eta (\epsilon_p - \epsilon_q)}{((\epsilon_p - \epsilon_q)^2 + \eta^2)^2} f(\epsilon_q) (1 - f(\epsilon_p)). \quad (6)$$

$f(\epsilon)$  denotes the Fermi-Dirac occupation numbers.

We have calculated conductances for molecules with only one site (single interacting level) and with five sites. We begin with the single level model with numerical parameters:  $t' = 0.1$ . The model enjoys a particle hole symmetry, so that the single transport resonance is pinned to the band center,  $E=0$ . Fig. 2 shows the exact,  $g(V_{\text{gate}})$ , and the Kohn-Sham conductance  $g_s$ . Comparison to the non-interacting limit ( $U=0$ ) exhibits a strong (280%) interaction driven enhancement of the resonance width,  $\Gamma = 0.116$ , compared to the non-interacting case  $\Gamma = 4t'^2 = 0.04$ . Exact DFT,  $g_s$ , is able to reproduce this renormalization effect with accuracy better than 10%,  $\Gamma^{\text{DFT}}=0.106$ .

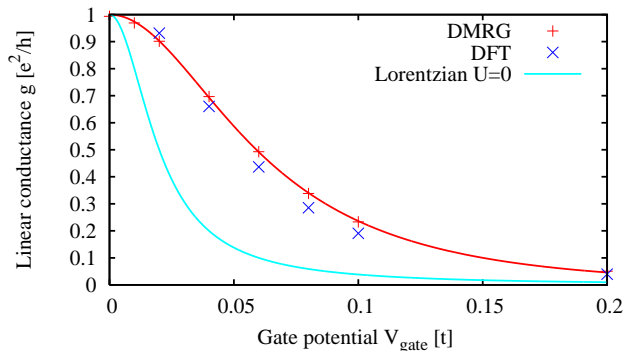


FIG. 2: (Color online) Linear conductance over the gate voltage for the IRLM model with  $t' = 0.1$ . Comparison of the conductance calculated within DMRG for the full problem (+) and for the corresponding effective DFT Hamiltonian ( $\times$ ). The line through the DMRG data is a guide to the eyes and the Lorentzian is the non-interacting result as reference. DMRG half width:  $\Gamma = 0.116 \pm 0.001$ ; DFT:  $0.106 \pm 0.002$ ; noninteracting system,  $U = 0$ : 0.04.

We now turn to the five site case, which affords four single levels, that are not pinned to zero energy. Since now resonances experience an occupation dependent and interaction driven shift (“Coulomb blockade”) with a corresponding change of the resonance width, this model can serve to investigate the DFT handling of such renormalization phenomena.

Fig. 3 displays the  $g(V_{\text{gate}})$  and  $g_s(V_{\text{gate}})$  conductance. Since particle-hole symmetry implies invariance under  $V_{\text{gate}} \leftrightarrow -V_{\text{gate}}$ , only the positive branch is shown. The first resonance at nonzero energy signalizes the transition, where the electron number  $N_{\mathcal{M}}(V_{\text{gate}})$  of the molecular dot changes between two and one, see Fig. 3. This happens at  $V_{\text{gate}} \sim U - \Delta$ , where  $\Delta$  denotes the single particle level spacing. This expectation is roughly consistent with the numerical value 1.8 obtained from Fig. 3, for details see [18].

Fig. 3 clearly shows, that the DFT calculation perfectly well captures the position of the transport resonances. In addition, the broadening of the resonance peaks is described reasonably well. Similar to the single level case, for the center peak width 10% deviations have to be accounted for. By contrast, a logarithmic plotting is required in order to make the relative deviations visible for the broadening of the shifted peaks. Remarkably, near resonances the variation of the conductivity is described over more than three orders of magnitude with deviations of a few percent or less.

In Fig. 4 we show the evolution of the local on site potential  $v^{\text{HXC}}$  with increasing gate voltage. The overall behavior is complicated, and a detailed discussion has to be relegated to Ref. [19]. Here, we can only briefly comment on two crucial aspects. First,  $v^{\text{HXC}}$  partially compensates  $V_{\text{gate}}$  for repulsive voltages inbetween two resonances, keeping  $N_{\mathcal{M}}$  integer, c. f. Fig. 3. Second, at the resonance,  $V_{\text{gate}} \approx 1.855$ , the center peak of Fig. 4

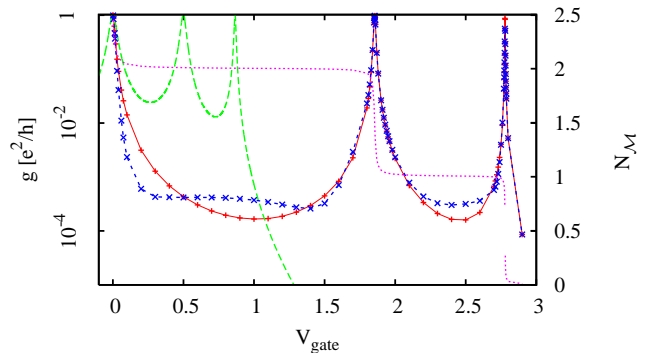


FIG. 3: (Color online) Comparison of the exact conductance (+) and the ground state DFT approximation ( $\times$ , dashed line as a guide) for a five site system ( $t' = 0.2$ ). For comparison the noninteracting  $U = 0$  is shown as well (long dashed line). Solid line indicates the particle number  $N_{\mathcal{M}}(V_{\text{gate}})$  the molecule. The resonance of  $g$  are sitting  $V_{\text{gate}} = 0, 1.854$ , and  $2.779$  with a resonance width of  $\Gamma = 0.026, 0.015$ , and  $0.0033$ .

rapidly decays. Thus, the double well structure in the full effective potential  $v^{\text{HXC}} + V_{\text{gate}}$ , that was appropriate for two repulsive particles  $N_{\mathcal{M}} = 2$ , transmutes into a single well hosting the lone particle,  $N_{\mathcal{M}} = 1$ .

The predictive power of conductance calculations with ground state DFT may seem surprising at first sight, because  $V_{\text{XC}}$  is neglected albeit it is very well known that the bare KS-response yields incorrect excitation energies, which are shifted to proper values in TDDFT only by including dynamical correlations.[20] A closely related fact: the bare KS-spectral function,  $A_s(\omega, V_{\text{gate}} = 0)$  exhibits excitation peaks at frequencies  $\omega$  of the order of  $\Delta$ , and not  $U$ . The point, that we wish to make here is, that for correlated electron systems the dependency of  $A_s$  on its arguments  $\omega$  and  $V_{\text{gate}}$  is quite different. The linear transport probes  $A_s$  only in the vicinity of zero frequency. The evolution of  $A_s(\omega = 0, V_{\text{gate}})$  with gate voltage is closely tied to the particle number and therefore can be physically meaningful and give quantitative results even if dynamical corrections are ignored.

We elaborate on this issue and give two reasons, why in fact the good performance of  $g_s$  is not entirely unexpected. (1) We are concerned with isolated resonances  $\Gamma \ll \Delta, U$ , which is a situation typical of the relatively small molecules that one deals with in the field of Molecular Electronics. These resonances occur precisely at the degeneracy point, where the  $N$  and  $N+1$  particle states of the molecular dot coincide in energy, so that the particle number is half integer  $N+1/2$ . Since the exact DFT monitors the true particle number on the dot, the degeneracy point of the KS-occupation and hence the KS-transport resonance coincide with the true value. (2) It is much less obvious, why also the resonance width  $\Gamma$  should always be given very accurately, and in fact there is no reason to believe that this is the case. However, under fairly general assumptions, one may argue that the width  $\Im \Sigma$  of the transition in  $N_{\mathcal{M}}(V_{\text{gate}})$  gives a very good es-

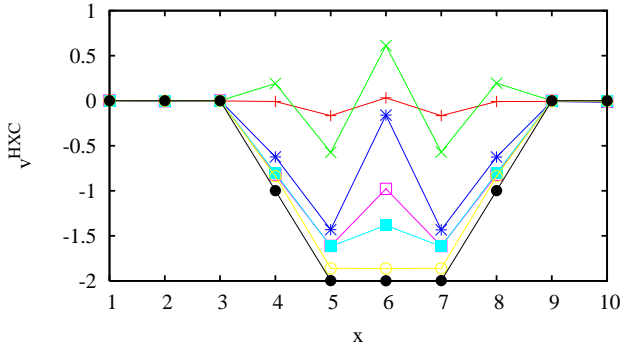


FIG. 4: (Color online) Potential  $v_l^{\text{HXC}}$  on sites  $l$  of  $e\mathcal{M}$  corresponding to conductance data shown in previous Fig. 3 at  $V_{\text{gate}}=0.2, 0.005, 1.5, 1.85, 1.86, 2.5, 2.8$  (labeling center site,  $x=6$ , from top to bottom).

estimate for the width  $\Gamma$  of the transport resonance. Indeed, consider a molecular dot invariant under exchange of left and right reservoirs (symmetric coupling). Then the single particle lifetime proper,  $\Im\Sigma^{-1}$ , of molecular excitations also appears as a transport rate  $\Gamma \approx \Im\Sigma$ , since the escape rates into the left and right leads,  $\Gamma_L$  and  $\Gamma_R$ , simply coincide with  $\Im\Sigma/2$ . Therefore  $\Gamma^{-1}$  sets the (only) time scale for relaxation processes and hence it should also describe the width of transport resonances. Notice, that  $N_{\mathcal{M}}(V_{\text{gate}})$  cannot easily distinguish two situations, where  $\Gamma_L$  and  $\Gamma_R$  are vastly different with the sum,  $\Gamma=\Gamma_L+\Gamma_R$ , being kept fixed. The excellent agreement found in this work for the symmetric case may no longer pertain into the strongly asymmetric limit, since  $g_s \propto \Gamma_L\Gamma_R$ .

In summary, we have presented a method for performing exact DFT calculations for model systems based on the density matrix renormalization group (DMRG). The approach has been used in order to calculate ground state Kohn-Sham conductances for the interacting resonant level model (IRLM), which can be compared to exact results obtained with DMRG. We find that DFT calculations can describe positions and broadenings of transport resonances with a very good accuracy. In fact, the resonance position will be given very precisely for any correlated electron system, as long as it is connected to a single resonant free fermion level by adiabatically switching on the interaction (Fermi liquid regime). A further implication suggested by our result is that dynamical corrections should be small as long as vertex corrections can be ignored. So the most pressing limitations in practical DFT conductance calculations appears to be the missing derivative discontinuity. This poses a notoriously difficult problem which, however, in principle has been well understood.[21]

Finally, we mention that our method DFT $\oplus$ DMRG is a very general approach, and not restricted to the IRLM employed in this work. It will an intriguing question

to be addressed in future work, to what extend DFT can capture also those phenomena – be it in the density response or in transport signatures – which live beyond the regime of attraction of the Fermi liquid fixed point.

Useful discussions with K. Burke, F. Furche, G. Schneider and P. Wölfle are gratefully acknowledged. This work was supported by the Center of Functional Nanostructures at Karlsruhe University.

- 
- [1] M. Brandbyge, J.-L. Mozoz, P. Ordejon, P. J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).
  - [2] F. Evers, F. Weigend, and M. Koentopp, Phys. Rev. B **69**, 235411 (2004).
  - [3] A. Arnold, F. Weigend, and F. Evers, J. Chem. Phys. **126**, 17401 (2007).
  - [4] G. Stefanucci and C.-O. Almbladh, Physical Review B **69**, 195318 (2004); Europhys. Lett. **67**, 14 (2004).
  - [5] M. Koentopp, K. Burke, and F. Evers, Physical Review B **73**, 121403(R) (2006); F. Evers and K. Burke, condmat/061013, Chapter 24 in the CRC Handbook on Molecular Electronics, ed. S. Lyshevski, 2007.
  - [6] R. M. Dreizler and E. K. U. Gross, *Density functional theory*, Springer-Verlag, 1990.
  - [7] N.T. Maitra, K. Burke, H. Appel, E.K.U. Gross and R. van Leeuwen, Rev. Mod. Quantum Chem. in *A Celebration of the Contributions of R.G. Parr*, K.D. Sen, ed(s) (World Scientific, 2002)
  - [8] For an explicit study with the bipyridine molecule, see A. Arnold, thesis U Karlsruhe (2007).
  - [9] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. **95**, 146402 (2005).
  - [10] S.-H. Ke, H. U. Baranger, and W. Yang, cond-mat/0609637v2.
  - [11] N. Sai, M. Zwolak, G. Vignale, and M. Di Ventra, Phys. Rev. Lett. **94**, 186810 (2005); Phys. Rev. Lett. **98**, 259702 (2007); J. Jung, P. Bokes, and R. W. Godby, Phys. Rev. Lett. **98** 259701 (2007).
  - [12] Density Matrix Renormalization – A New Numerical Method in Physics, ed. by I. Peschel, X. Wang, M.Kaulke, and K. Hallberg, Springer (1999); R. M. Noack and S. R. Manmana, AIP Conf. Proc. 789, 93-163 (2005)
  - [13] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992); Phys. Rev. B **48**, 10345 (1993).
  - [14] D. Bohr and P. Schmitteckert, Phys. Rev. B **75** 241103(R) (2007)
  - [15] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **56**, 1968 (1986)
  - [16] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)
  - [17] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)
  - [18] D. Bohr, P. Schmitteckert and P. Wölfle, Europhys. Lett. **73**, 246 (2006)
  - [19] P. Schmitteckert and F. Evers, to be published.
  - [20] G. Stefanucci, S. Kurth, E.K.U. Gross, and A. Rubio, in *Molecular and nano electronics: analysis, design and simulation*, J. Seminario, ed(s) Elsevier Series on Theoretical and Computational Chemistry 247, **17** (2007)
  - [21] *The ABC of DFT*, Lecture notes by K. Burke (unpublished)